

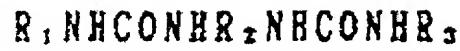
UREA GREASE COMPOSITION

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Abstract of JP1139696

PURPOSE: To obtain the title composition having excellent mechanical stability at high temperature, low thermosetting tendency and extremely excellent acoustic characteristics, by compounding a mineral oil or synthetic oil with a specific amount of a thickening agent produced by mixing two specific kinds of diurea compounds at a specific ratio.

CONSTITUTION: The objective composition can be produced by compounding a mineral oil or a synthetic oil with 2-30wt.% of a thickner consisting of a mixture of (A) 95-10mol% of a diurea compound of formula I (R1 and R3 are saturated 8C alkyl; R2 is diphenylmethane residue) and (B) 5-90mol% of a diurea compound of formula II (R4 and R6 are alkyl-substituted aromatic group or halogen-substituted aromatic group; R5 is tolylene or bitolyene).



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(54) UREA GREASE COMPOSITION

(57)Abstract:

PURPOSE: To obtain the title composition having excellent mechanical stability at high temperature, low thermosetting tendency and extremely excellent acoustic characteristics, by compounding a mineral oil or synthetic oil with a specific amount of a thickening agent produced by mixing two specific kinds of diurea compounds at a specific ratio.

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R-NHCONHR-NHCONHR

R-NHCONHR-NHCONHR

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[WHAT IS CLAIMED IS:]

[Claim 1]

Nitramine, (a) $R_1 \text{NHCONHR}_2 \text{NHCONHR}_3$ (b) $R_4 \text{NHCONHR}_5 \text{NHCONHR}_6$ (out of equation, as for R_2 , as for diphenyl-methane group, R_1 and R_3 , linear of carbon number 8 or branching-shaped saturation alkyl group, R_5 show each alkylation aromatic group or halogenation aromatic group in tolylene radical or bitoriren radical, R_4 and R_6 respectively.) It is compost of the diurea compound which it appears, and is made to hyowa, and it is composition of urea grease including 2-30 % by weight containing the thickener which is blending ratio of coal 5 of component (b) - 90 mol %, blending ratio of coal 95 of constituent (a) - ten mol % as against liquid petrolatum or synthetic oil.

[DETAILED DESCRIPTION OF THE INVENTION]

The field of industrial application present invention relates to a diurea grease composition. In particular, The present invention relates to diurea grease composition of the high quality which high drip-point is provided and is superior in mechanical soundness in high temperature, and there is a very little thermosetting property, and acoustic properties are full of, and is good. There is a prior-art thing described for literature about diurea grease conventionally by Japanese Patent Publication No. 46-4489, for example,, general formula $R \text{NHCONHR}^1 \text{NHCONHR}$ (as for R^1 , aromatic hydrocarbon group of 2 values, R show cycloalkyl group out of equation.) It attends and is made to hyowa. As for aromatic hydrocarbon group of 2 values, R_2 , R_3 , the thing which there is in diurea system grease having alkyl group of cyclohexyl group or $C_7 \dots C_{12}$ cyclohexyl derivative radical or $C_8 \dots C_{12}$ which of end of diurea cyclohexyl group or the derivative and alkyl group are in is disclosed to R_1 in nitramine $R_2 \text{NHCONHR}_1 \text{NHCONHR}_3$ to Japanese Patent Publication No. 55-11156. In addition, Tolylene diisocyanate and para toluidine, the diurea chemical agent which, even more particularly, assume tolylene diisocyanate and para toluidine, para chloroaniline constituent to a tertiary ,082,170 are disclosed to *bitorirenjiisoshianeto* and para toluidine, diurea compound comprising of para chloroaniline, a tertiary ,374,170 to U.S. Patent No. 3,563,894. As for low noise urea grease, there is the diurea system grease which improved the noise that inclusion succeeds in getting higher than one kind or two kinds, and it is of alkenyl succinimide, alkylbenzene sulfonic acid metal salt and petroleum sulfonic acid metal salt to Japanese Patent Laid-Open No. 58-185693. Heat resistance, oxidation resistance stability are given as feature of the lubricating grease which did an increase butterfly in the problems urea compound that invention is going to be settled, is expected as grease for high temperature longlivedness. However, As for the marketed urea grease, there is issue in a hardening phenomenon in a high temperature bottom and mechanical soundness, the point which should be improved is recognized. In addition, Urea grease can employ in high temperature as compared to lithium system grease for a long time, but, acoustic properties are bad, and *hotondo n* cannot be employed terribly in the point where low noise is called for. On the other hand, It becomes very too cruel, and application environment of grease can employ in high temperature with miniaturization and speedup of equipment for a long time and a superior thing is expected from noise low. As a result that, even more particularly, stability of thermosetting property under the high temperature that the present invention was considered to be shortcoming about this urea grease conventionally and machine studied betterment of acoustic properties, urea grease having extremely good macromolecular chromophore was able to be developed. The measure present invention to solve problems is compost of diurea compound expressed with nitramine (a) $R_1 \text{NHCONHR}_2 \text{NHCONHR}_3$ (b) $R_4 \text{NHCONHR}_5 \text{NHCONHR}_6$ (linear of carbon number 8 or branching-shaped saturation alkyl group, R_5 show each alkylation aromatic group or halogenation aromatic group in tolylene radical or bitoriren radical, R_4 and R_6 as for diphenyl-methane group, R_1 and R_3 as for R_2

out of equation respectively), and urea grease composition including 2-30 % by weight containing the thickener which is blending ratio of coal 5 of component (b) - 90 mol %, blending ratio of coal 95 of constituent (a) - ten mol % as against liquid petrolatum or synthetic oil is related to. Much diurea grease is usually chemical agent comprising of reaction with diisocyanate and the first grade amine in lube oil, but, it is different much grease make by choosing class of isocyanate and amine and various kinds of characteristic is massive. By way of example only, If alkyl monoamine 2mol is used as against diisocyanate 1mol, if both terminal group uses allyl monoamine 2mol for alkyl group or diisocyanate 1mol, both terminal group suffers from allyl group. In addition, If alkyl monoamine 1mol and allyl monoamine 1mol are used as against diisocyanate 1mol, both end can make the grease which an alkyl group and allyl group are introduced into respectively. As thus described diurea grease separates greatly, and three kinds of form is given in configuration. In general terms, the diurea grease which assumes an alkyl group terminal group compares allyl group with terminal group and diurea grease doing, and oxidation resistance stability and heat resistance are inferior, but, it is tended to be superior in stability of butterfly degree yield and machine. However, This is gravitation generic to the last, and terminal group and all diurea grease doing are not superior in stability of just at yield and machine in an alkyl group, all of terminal group and diurea grease doing is not superior in heat resistance in alkyl group. There are many a thing showing flow condition and thing number to show a remarkable heat curing phenomenon in inside. As thus described ability of grease is massive, and natural many ability can vary from to by what a change and class of isocyanate are changed into by class of amine when diisocyanate was limited to one kind. This researchers produce much diurea grease experimentally, as a result of it was examined, and having examined, it is high drip-point and there is a little heat curing in high temperature and is superior in stability of heat resistance and machine, even more particularly, superior diurea grease was found in acoustic properties. In other words, R_1 of component (a) and R_3 is linear or branching-shaped saturation alkyl group in diurea compound expressed with equation (a) R_1 NHCONHR_2 NHCONHR_3 (b) R_4 NHCONHR_5 NHCONHR_6 , and R_2 is diphenyl-methane radical, and R_4 of constituent (b) and R_6 are alkylation aromatic group or halogenation aromatic group, and R_5 is tolylene radical or *bitoriren* radical. Urea grease composition of the present invention is compost with component (a) and component (b), and it is 2 - 30 % by weight, the thing which made preferably contain 5 - 20 % by weight as against the base oil which is liquid petrolatum and synthetic oil as thickener in the diurea chemical agent which 95 - ten mol % includes 5 - 90 mol %, constituent (a) in in constituent (b), and it is grease of extremely superior ability. In addition, When there is a more little proportion 5 of component (b) than mol %, there is a little effect of blending application with component (a) and constituent (b) and is unfavorable from point of butterfly degree yield when rate 90 of on the other hand constituent (b) goes over mol %. R_2 is diphenyl-methane group grease of the present invention, and R_4 and R_6 is diurea grease limited to terminal group and diurea chemical agent doing coexisting within equivalence thickener in alkylation aromatic group or halogenation aromatic group in tolylene radical or *bitoriren* radical terminal group and diurea chemical agent and R_5 doing in octyl radical R_1 and R_3 , but, even if R_4 and R_6 or R_5 are converted to chemical agent aside from superscription in R_1 and R_3 or R_2 range, and diurea grease is made, it is ineffective in in ability at all. By way of example only, As for R_1 and the diurea grease that R_3 is octyl group, and R_2 is expressed in tolylene group or *bitoriren* group, comparing unfavorably, stability of machine are bad in just at yield. In addition, R_1 and R_3 is carbon number 10 - 18 alkyl group, and, as for the most of the diurea grease which R_2 is tolylene group or *bitoriren* group - diphenyl-methane radical, and is expressed, stability of machine in high temperature is bad. Even more particularly, R_4 and R_6 is alkylation aromatic group or halogenation aromatic group, and, as for the diurea grease that R_5 is expressed in diphenyl-methane group, acoustic properties are very bad. As for the grease of the present invention, the shortcoming that component (a) independent shortcoming and constituent (b) are isolated is removed in complete by component (a) and putting component (b) together. By way of example only, Diurea grease

including constituent expressed in R_1 and diphenyl-methane group of octyl group and R_2 of R_3 (a) is isolated, and, even more particularly, acoustic properties are superior stability of increase butterfly effect and machine, but, when thickener quantity reduces, depression of drip-point is recognized. On the other hand, R_4 and R_6 is alkylation aromatic group or halogenation aromatic group, and diurea grease including constituent expressed in tolylene group or *bitoriren* radical (b) is isolated, and R_5 is drip-point high and is stable in extremely as against heat, and comparable acoustic properties are preferable. However, There is shortcoming inferior to butterfly degree yield and mechanical soundness. Diurea grease of the extremely superior ability which drew superior ability of neither in maximum because these make the component which is component of thickener of both grease (a) and constituent (b) are put together, and coexist within equivalence thickener is provided. In addition, Various additive such as oxidation inhibitor, anti-rust agent, extreme pressure agent and abrasion proof agent may be added to improve ability of this lubricating grease more. Diurea grease of the present invention comprises high drip-point, now there is a little gravitation stiffening under high temperature in comparison with marketed urea grease and is superior in stability of machine and acoustic properties. As follows, Embodiment is advocated, and the present invention is explained. In addition, Comparative examples are written jointly, character of urea grease of the present invention was clarified. Base oil of diisocyanate and 60 part by weight of component (b) is put in grease kettle in blending ratio of coal shown in embodiment table 1, it heats to about 80 degrees Celsius, after having dissolved diisocyanate, it is drastic, and aromatic amine of the constituent which made this dissolve in base oil of 20 part by weight (b) is stirred as well as gradual. After, about 10 minutes later, having added 4,4 diphenyl-methane diisocyanate of component (a), the octyl amine which made base oil of 20 part by weight dissolve is added, and stirring is continued. Temperature rises by reaction with diisocyanate and amine, but, it makes, in this state, 170 degrees Celsius are heated to after stirring, and conclude reaction for about 30 minutes. Afterwards, *ho* cold water was kneaded to room temperature, and grease was made. The poly alpha-olefin oil that viscosity of mineral oil shown in embodiment is 11cst (100 degrees Celsius) is 12cst (100 degrees Celsius). Resultant of sound examination was shown in table 1 in butterfly degree (25 degrees Celsius, non-misce) range after a butterfly degree, drip-point of grease of each embodiment, shell roll (150 degrees Celsius, 24h) and heat in 180 degrees Celsius. In addition, Additive such as oxidation inhibitor, anti-rust agent is added to grease of example 1, and grease is made (example 1 0), the resultant which it was compared with commercial urea grease, and was examined was shown in table 2. In addition, Urea grease tetraarticle A commercial in table 2 (trade name made by AMOCO:) RICON1364), commercial article B, alicycle group diurea grease (trade name made in Nippon Oil:) paironokkuyunibasaru 2), commercial article C, aromatic diurea grease (trade name made by N O K kuryuba:) It was N O K kuryuba BT 280). Enter grease kettle, and 80 part by weight of diisocyanate and mineral oil is heated to about 80 degrees Celsius in blending ratio of coal shown in comparative example table 3 and table 4, after having dissolved diisocyanate, the amine which made dissolve in liquid petrolatum of 20 part by weight was added, and it was stirred. After, in this state, having continued a churn for about 30 minutes, it makes about 170 degrees Celsius are heated to, and reaction conclude, it was kneaded after *horei* in room temperature, and grease was made. And attribute table 3 of each comparative example was shown to table 4.

第 1 表

実施例		1	2	3	4	5	6	7	8	9
成分(a)	ジフェニルメタン4,4'-ジイソシアネート g	8.98	6.08	3.09	6.69	5.84	6.40	5.92	6.49	8.
	オクチルアミン08 g	9.29	6.29	3.19	6.92	6.04	6.62	6.11	6.71	9.
成分(b)	3,3'-ビトリレーン4,4'-ジイソシアネート g	3.16	6.42	9.79		6.17		6.25		3.
	(2,4/2,6(65%/35%))-トリレンジイソシアネート g				4.66		4.45		4.52	
	パラトルイジン g	2.57	5.21	7.93	5.73					2.

実施例		1	2	3	4	5	6	7	8	9
	パラクロロアニリン g					5.95	6.53			
	メタキシリジン g							5.72	6.28	
鉱油	g	176	176	176	176	176	176	176	176	176
	g									
ポリα-オレフィン	g									
増ちょう剤含有量	%	12	12	12	12	12	12	12	12	12
(a)/(b)	モル% / モル%	75/25	50/50	25/75	50/50	50/50	50/50	50/50	50/50	50/50

【性状】

ちよう度 (25°C、混和)	270	285	295	290	292	298	278	290	
滴点 °C	>260	>260	>260	>260	>260	>260	>260	>260	>260
シェルロール (150°C、24h)	283	296	325	341	359	361	355	357	
150°C加熱後ちよう度(25°C、不混和)	178	175	174	177	148	193	117	181	
音響試験 (120秒後)	52	59	67	48	38	50	41	40	

第 2 表

グリース 実施例 項目	10	市販品A	市販品B	市販品C
ちよう度 (25°C、混和)	275	237	270	295
滴点(°C)	>260	233	>260	>260
シェルロール (150°C、24h)	291	>440	233	335

グリース 実施例 項目	10	市販品A	市販品B	市販品C
150°C 加熱後ちよう度 (25°C、不混和)	189	102	92	129
音響試験 (120秒後)	61	>10,000	>10,000	2,135

第 3 表

比較例 項目	1	2	3	4	5	6	7	8	9
アミンの種類	カブリルアミン (C ₁₁)	ラグリルアミン(C ₁₂)	ミリスチルアミン (C ₁₃)	ステアリルアミン (C ₁₈)	オレイルアミン (C ₁₇)				
アミン	12.20	14.84	17.91	18.94	21.32	20.41	22.60	20.26	22.
ジブチルメターン-4,4'-ジイソシアネート	11.80			11.06		9.59		9.74	
3,3'-ビトリレン-4,4'-ジイソシアネート		15.16	12.09						
[(2.4/2.6(65%/35%))ト-トリレンジイソシアネート					8.68		7.40		7.
鉱油 g	176	170	170	170	170	170	170	170	170
増ちよう剤含有量 g	12	15	15	15	15	15	15	15	15
〔性状〕									
ちよう度 (25°C、混和)	265	374	356	>400	384	231	341	232	
滴点 (°C)	221	>260	>260	>260	160	>260	177	>260	
シェルロール (150°C、24h)	277	>440	>440	>440	>440	>440	>440	423	>

比較例 項目	1	2	3	4	5	6	7	8	9
150°C加熱後ちよう度(25°C、不混和)	185	212	215	60	103	80	90	60	
音響試験 (120秒後)	51	59	205	>10,000	45	149	49	335	

第 4 表

項目	比較例	10	11	12	13	14	15	16
アミンの種類			アニリン		ベンジルアミン			パラトライジン
アミン g		12.80	12.40	15.50	13.84	13.43	13.45	13.
ジフェニルメタン-4,4'-ジイソシアネート g		17.20			16.16			16.
3,3'-ビトリレン-4,4'-ジイソシアネート g			17.60			16.57		
[2,4/2,6(65%/35%)]-トリレンジイソシアネート g				14.50			16.55	
鉛油 g		170	170	170	170	170	170	170
増ちょう剤含有量 %		15	15	15	15	15	15	15
(性状)								
ちょう度 (25°C、混和)		>400	367	>400	387	371	385	
滴点 (°C)		>260	>260	>260	>260	>260	>260	>260
シェルロール (150°C、24h)		>440	>440	>440	>440	>440	>440	>440
150°C加熱後ちょう度 (25°C、不混和)		140	73	122	197	127	158	
音響試験 (120秒後)		>10,000	>10,000	>10,000	>10,000	>10,000	>10,000	>10,000

項目	比較例	17	18	19	20	21	22	23	24
アミンの種類		パラトライジン		パラクロロアニリン		メタキシリジン			
アミン g		13.43	13.45	15.15	14.74	17.83	14.75	14.34	17.
ジフェニルタクシ-4,4'-ジイソシアネート g				14.85			15.25		
3,3'-ビトリレン-4,4'-ジイソシアネート g		16.57			15.26			15.66	
[2,4/2,6(65%/35%)]-トリレンジイソシアネート g			16.55			12.17			12.
鉛油 g		170	170	170	170	170	170	170	170
増ちょう剤含有量 %		15	15	15	15	15	15	15	15
(性状)									
ちょう度 (25°C、混和)		351	365	384	374	385	347	337	
滴点 (°C)		>260	>260	>260	>260	>260	>260	>260	>260
シェルロール (150°C、24h)		373	414	>440	>440	>440	>440	>440	>440
150°C加熱後ちょう度 (25°C、不混和)		152	174	272	99	215	137	49	
音響試験 (120秒後)		133	247	>10,000	240	585	725	239	

The measuring method of check article was done according to the next method. A butterfly degree: - 2220 drops JIS K point: JIS K -2220 shell roll: It is a butterfly degree after ASTM D 1831150 degrees Celsius heat: In accordance with JIS K -2220, checkmate grease in 1/4 consistency measuring instrument, and it is cooled off after heat for 150 degrees Celsius, 72 hours, non-misce butterfly degree in 25 degrees Celsius was measured. Sound check: Bearing noise meter numerical value was measured about each grease by means of sound testing machine NSK GREASE NOISE TESTER on the basis of Japanese Patent Publication No. 53-2357 (title of the invention "measuring method of quantity of solid debris coexisting in grease, applicant" Nippon Seiko K. K.) (a product made in Nippon Seiko K. K.). If effect of the invention advantage offered by the invention is shown, as follows. (1) Urea grease of the present invention is high drip-point, and mechanical soundness in a high temperature bottom is good remarkably. (2) Urea grease of the present invention is exposed to a high temperature bottom for a long time, and configuration of grease is stable in extremely, and there is a little hardening phenomena by heat. (3) Urea grease of the present invention comprises the superior acoustic properties which conventional urea grease does not have.

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